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Pyrotechnic composition for producing IR-radiation

10                The invention concerns a pyrotechnic composition for producing IR-radiation.

                  Missiles are used in the military sphere for combating aerial targets such as for example jet aircraft, helicopters and transport aircraft, the missiles locking on to and tracking the infrared(IR)-radiation emanating  
15                from the propulsion unit of the target, principally in the range of between 0.8 and 5  $\mu\text{m}$ , by means of a seeker head which is sensitive to IR-radiation. Therefore to provide a defence against such missiles use is made of deception units (referred to as flares) which imitate the IR-signature of the target.

20                A large number of pyrotechnic compositions are already known from the state of the art, which can be used for IR-deception units for producing IR-radiation.

                  For example US-A-5 679 921 discloses a pyrotechnic composition comprising magnesium, polytetrafluoroethylene (PTFE, commercially  
25                available under the trade name Teflon®) and polytrifluorochloroethylene (commercially available under the trade name Kel-F®). A similar pyrotechnic composition is known by the abbreviation MTV and comprises magnesium, Teflon® and Viton® (trade mark for hexafluoropropene-vinylidene difluoride copolymer from DuPont). When they burn MTV compositions of that kind  
30                predominantly produce magnesium fluoride and carbon black. The effectiveness of deception units containing MTV compositions against IR-seeking heads is based on the one hand on the high heat of formation of the magnesium fluoride and on the high level of emissivity of the carbon

black produced which, due to the thermal stimulation, exhibits almost black body radiation.

EP 0 948 735 B1 further discloses an extrudable flare material with black body characteristics, which includes magnesium, PTFE and a  
5 polyaromatic thermoplastic binding agent (for example comprising polystyrene and a plasticiser). US-A-5 531 844 describes a pyrotechnic composition with a mixture comprising a metal (preferably aluminium) and perfluorinated polyether (PFPE) and finally EP 1 090 895 A1 describes a  
10 pyrotechnic composition with graphite fluoride as an oxidation agent and a metal (preferably magnesium) as fuel.

While, in the above-mentioned cases, the fluorine-furnishing oxidation agent PTFE or graphite fluoride is used as the carbon source for the desired black body characteristic, US-A-5 834 680 describes a  
15 pyrotechnic composition which contains a metal (magnesium or aluminium), ammonium perchlorate and a polyaromatic compound (decacyclene, anthracene or naphthalene), upon the combustion of which graphite-like firing products are produced.

There is now a persistent interest in increasing the power of pyrotechnic compositions for IR-deception bodies.

20 The object of the present invention is therefore that of providing a pyrotechnic composition having a markedly increased level of power while retaining the spectral black body characteristic.

In accordance with the invention that object is attained by a pyrotechnic composition having the features of claim 1. Preferred  
25 configurations and developments of the pyrotechnic composition according to the invention are recited in the appendant claims.

The pyrotechnic composition according to the invention contains as oxidation agent fluorinated, spherical, carbocyclic cage molecules or  
30 polymers with such fluorinated cage molecules as monomers and as fuel it contains a halophilic metal which combines with fluorine in an exothermic reaction or a metal alloy of that nature. The specified fluorinated spherical, carbocyclic cage molecules have a formation enthalpy which is markedly lower in comparison with the conventionally employed PTFE or graphite

fluoride and/or a considerably increased reactivity, which results in a considerable increase in the power or radiation density of the pyrotechnic composition.

By virtue of such an increase in power it is possible for example to achieve the same power with smaller amounts of pyrotechnic active materials, whereby it is possible to reduce the risk of explosion and fire in the course of manufacture. In addition, the IR-deception bodies can be made smaller and lighter by virtue of a reduction in the pyrotechnic active material and thus the deception body capacity of aircraft can be increased.

In accordance with a first aspect of the invention the oxidation agents used are fluorinated spherical, carbocyclic cage molecules of the general formula  $(CR^F)_n$  with  $R^F = C_mF_{2m+1}$  or polymers with such fluorinated cage molecules as monomers, wherein  $n$  is a natural number and  $m$  is a natural number including 0. In that respect, the oxidation agent used is preferably an above-specified fluorinated cage molecule with the parameters  $m = 0$  (that is to say  $R^F = F$ ) or  $m = 1$  (that is to say  $R^F = CF_3$ ) and with  $n = 4, 6, 8, 20, 60$  or  $70$ . Examples of such oxidation agents according to the invention are tetrafluorotetrahedrane  $(CF)_4$ , tetrakis(trifluoromethyl)tetrahedrane  $C_4(CF_3)_4$ , hexafluoro[3]-prismane  $(CF)_6$ , hexakis(trifluoromethyl)[3]-prismane  $C_6(CF_3)_6$ , octafluorocubane  $(CF)_8$ , octakis(trifluoromethyl)cubane  $C_8(CF_3)_8$  and eicosafluorododecahedrane  $(CF)_{20}$ .

In accordance with a second aspect of the invention the oxidation agents used are polyfluorofullerenes of the general formula  $C_{60+2n}F_{2m}$  or polymers with such polyfluorofullerenes as monomers, wherein  $n$  is a natural number including 0 and  $m$  is a natural number.

Examples of such oxidation agents according to the invention which have already been tried in tests are [60]-fluorofullerene- $C_{60}F_{48}$  and [60]-fluorofullerene- $C_{60}F_{60}$ .

In accordance with a third aspect of the invention the oxidation agents used are polyfluorofullerenes of the general formula  $C_{60+2n}R^1_mR^2_bZ_y$  or polymers with such polyfluorofullerenes as monomers, wherein  $R^1$  is a straight or branched hydrocarbon chain or an aromatic radical with up to

100 carbon atoms,  $R^2$  is a straight or branched fluoroalkyl with up to 100 carbon atoms and Z is a hydrogen, fluorine or chlorine atom, and wherein n, m and y are natural numbers including 0 and b is a natural number.

Suitable metals for the fuel of the pyrotechnic composition according to the invention are for example metals from the group of metals lithium, beryllium, magnesium, zinc, calcium, strontium, barium, boron, aluminium, titanium, zirconium, hafnium or a mixture or alloy of those metals. Magnesium is particularly preferred as the fuel because of its availability and costs.

In accordance with a further configuration of the invention the molar stoichiometry of the pyrotechnic composition preferably complies with the formula  $\Phi/M \leq w$ , wherein  $\Phi$  is the number of fluorine atoms per fluorinated cage molecule or monomer, M is the number of metal atoms and w is the maximum degree of oxidation of the metal. In other words the metal should preferably be contained over-proportionally with respect to the fluorine as, by virtue of the high thermal conductivity of the metals, that leads to higher reaction rates on the part of the pyrotechnic composition.

In still a further embodiment of the invention the oxidation agent can be sublimed on to the metal for example by means of gaseous phase deposition.

The invention is based on the considerations described hereinafter.

The power or the specific radiation density  $I_\lambda$  of pyrotechnic compositions or active materials for producing IR-radiation is given in accordance with equation (1) by the mass throughput  $\dot{m}$  (in  $\text{g}\cdot\text{s}^{-1}\cdot\text{cm}^{-2}$ ) and the specific power  $E_\lambda$  (in  $\text{J}\cdot\text{g}^{-1}\cdot\text{s}^{-1}$ ):

$$I_\lambda = \dot{m} \cdot E_\lambda \quad (1)$$

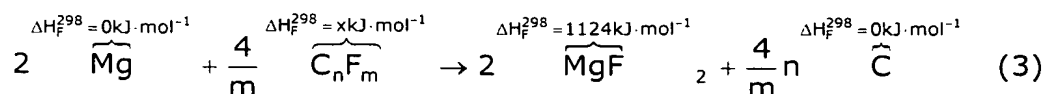
The power of the pyrotechnic composition can thus be increased both by an increased mass throughput  $\dot{m}$  and also by an increased specific power  $E_\lambda$ .

In order to increase  $E_\lambda$  in the case of a given metallic fuel such as for example magnesium for example the formation enthalpy  $\Delta H_F^{298}$  (in  $\text{kJ}\cdot\text{mol}^{-1}$ ) of the fluorocarbon which is used can be reduced in comparison with

conventional fluorine-providing oxidation agents such as PTFE or graphite fluoride. That is due to the fact that the specific power  $E_\lambda$  in accordance with the following equation (2), is directly proportional to the reaction enthalpy  $\Delta H_R$  (in  $\text{kJ}\cdot\text{mol}^{-1}$ ) [1]:

$$E_\lambda = \frac{1}{4\pi} \cdot \Delta H_R \cdot \frac{1}{\varepsilon \sigma T^4} \cdot \int \frac{\varepsilon_\lambda C_1}{\lambda^5} \cdot \frac{1}{\exp\left(\frac{C_2}{\lambda T}\right) - 1} d\lambda \quad (2)$$

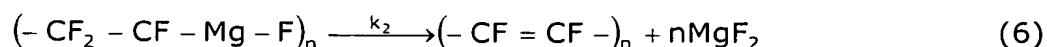
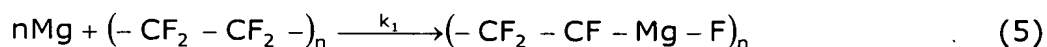
and that for the system selected by way of example, magnesium/fluorocarbon, for which the following reaction equation (3) applies:



the reaction enthalpy  $\Delta H_R$  is determined in accordance with the following equation (4):

$$\Delta H_R = 2 \cdot (-1124 \text{ kJ}\cdot\text{mol}^{-1}) - \frac{4}{m} \cdot x \text{ kJ}\cdot\text{mol}^{-1} \quad (4)$$

At the same time the mass throughput  $\dot{m}$  can be increased if more reactive fluorocarbons are used as the oxidation agent. That is due to the fact that the speed constant  $k_1$  for a pre-firing reaction [2] when firing magnesium/PTFE-active charges in the condensed phase in accordance with the reaction equations (5) and (6):



is determined in accordance with the Arrhenius equation (7):

$$k = A \cdot \exp\left(-\frac{E_a}{R \cdot T}\right) \quad (7)$$

by the activation energy  $E_a$  (in  $\text{kJ}\cdot\text{mol}^{-1}$ ) of the insertion reaction of the magnesium into the C-F-bond. That behaviour can also be transferred to other magnesium/fluorocarbon systems, for which then also the mass throughput  $\dot{m}$  is determined by the activation energy  $E_a$  of the insertion step in accordance with equation (5).

The activation energy  $E_a$  has already been investigated for various Mg-insertion reactions in fluorocarbon compounds of the type of equation

(5) [3, 4, 5]. In accordance therewith the reaction speed rises for the fluorocarbons set forth hereinafter in the sequence:



5 It is to be noted overall that an increase in the power of IR-active materials can be achieved by using as the oxidation agents fluorine compounds which have a lower formation enthalpy  $\Delta H_F^{298}$  and/or an increased level of reactivity than conventionally used oxidation agents.

10 The following Table shows, for various fluorinated spherical, carbocyclic cage molecules which in accordance with the present invention can advantageously be used as oxidation agents, and in comparison therewith, for the conventional oxidation agents PTFE and graphite fluoride, the formation enthalpies  $\Delta H_F^{298}$  known from the literature, and the reaction enthalpies  $\Delta H_R$ , ascertained in accordance with equations (3) and (4), in respect of the reactions of the respective oxidation agents with magnesium.

15 The right-hand column additionally gives the difference in the reaction enthalpies  $\Delta H_R$  between the reactions with the respective oxidation agents x and with the PTFE conventionally used as an oxidation agent.

Oxidation agent	Formula	$\Delta H_F^{298}$ [kJ·mol <sup>-1</sup> ]	$\Delta H_R$ [kJ·mol <sup>-1</sup> ]	$\Delta H_R \text{ Mg+x) -}$ $\Delta H_R \text{ (Mg +}$ $\text{PTFE)}$ [kJ·mol <sup>-1</sup> ]
PTFE [6]	$(-C_2F_4-)_n$	- 809.60	- 1,438.40	0.00
Graphite fluoride [7]	$(-CF-)_n$	- 195.00	- 1,468.00	- 29.60
Tetrafluorotetrahedrane [8]	$(CF)_4$	- 0.42	- 2,247.58	- 809.18
Tetrakis(trifluoromethyl)- tetrahedrane [8]	$C_4(CF_3)_4$	- 1,945.00	- 1,599.67	- 161.27
Hexafluoro[3]-prismane [8]	$(CF)_6$	- 459.00	- 1,942.00	- 503.60
Hexakis(trifluoromethyl)-[3]- prismane [9]	$C_6(CF_3)_6$	- 3,592.00	- 1,449.78	- 11.38
Octafluorocubane [10]	$(CF)_8$	- 518.00	- 1,989.00	- 550.60
Octakis(trifluoromethyl)- cubane [11]	$C_8(CF_3)_8$	- 4,401.00	- 1,514.50	- 76.10
Eicosafluorododecahedrane [12]	$(CF)_{20}$	- 2,905.00	- 1,667.00	- 228.60
[60]-Fluorofullerene- $C_{60}F_{48}$ [13]	$C_{60}F_{48}$	- 7,563.00	- 1,617.75	- 179.35
[60]-Fluorofullerene- $C_{60}F_{60}$ [14]	$C_{60}F_{60}$	- 5,895.00	- 1,855.00	- 416.60

As can be seen from the foregoing table except for the oxidation agent  $C_6(CF_3)_6$  all oxidation agents according to the invention in the reaction with magnesium afford a markedly higher level of combustion heat than the conventional oxidation agents PTFE and graphite fluoride.

Fluorine compounds with a low formation enthalpy  $\Delta H_F^{298}$  are for example fluorinated spherical, carbocyclic cage molecules of the general stoichiometric formula  $(CR^F)_n$ , with  $R^F = C_mF_{2m+1}$ . Suitable compounds of that kind are for example the following, set out in the Table: tetrafluorotetrahedrane  $(CF)_4$  with  $\Delta H_F^{298} = -0.4184$ , kJ·mol<sup>-1</sup> [6], tetrakis(trifluoromethyl)tetrahedrane  $C_4(CF_3)_4$  with  $\Delta H_F^{298} = -1,945$  kJ·mol<sup>-1</sup> [6], hexafluoro[3]-prismane  $(CF)_6$  with  $\Delta H_F^{298} = -459$  kJ·mol<sup>-1</sup> [6], hexakis(trifluoromethyl) [3]-prismane  $C_6(CF_3)_6$  with  $\Delta H_F^{298} = -3,592$  kJ·mol<sup>-1</sup> [7], octafluorocubane,  $(CF)_8$  with  $\Delta H_F^{298} = -518$  kJ·mol<sup>-1</sup> [8], octakis(trifluoromethyl)cubane  $C_8(CF_3)_8$  with  $\Delta H_F^{298} = -4,401$  kJ·mol<sup>-1</sup> [9] and eicosafluorododecahedrane  $(CF)_{20}$  with  $\Delta H_F^{298} = -2,905$  kJ·mol<sup>-1</sup> [10].

Further suitable oxidation agents according to the invention are polyfluorofullerenes of the general composition  $C_{60+2n}F_{2m}$ , such as for example, as set out hereinbefore in the Table, [60]-fluorofullerene- $C_{60}F_{48}$  with  $\Delta H_F^{298} = -7,563 \text{ kJ}\cdot\text{mol}^{-1}$  [11] and [60]-fluorofullerene- $C_{60}F_{60}$  with  $\Delta H_F^{298} = -5,895 \text{ kJ}\cdot\text{mol}^{-1}$  [12]. Polyfluorofullerenes of that kind can be produced by the most widely varying procedures with very good yields from the fullerenes  $C_{60+2n}$  (see for example DE 195 18 005 A1, and US No 6 386 468 B1).

Besides those derivatives of the fullerene  $C_{60+2n}$  in which the fluorine atoms are bound directly to the cage carbon atoms, fullerene derivatives which carry fluorinated side chains are also known. Those derivatives of the general composition  $C_{60+2n}R^1_mR^2_bZ_y$ , wherein  $R^1$  can be a straight or branched hydrocarbon chain or an aromatic radical with up to 100 carbon atoms,  $R^2$  is a straight or branched fluoroalkyl with up to 100 carbon atoms and Z can be an atom such as H, F and Cl, with  $n = 0 - 470$ ,  $m = 0$  to  $\sim 24+n$ ,  $b = 1$  to  $\sim 24+n$  and  $y = 0 - 35+b$ , are also suitable oxidation agents in accordance with the present invention and in the meantime are also available in high yields (see for example US-A-5 354 926).

It should also be expressly noted once again at this point that, besides the above-listed fluorinated spherical carbocyclic cage molecules of the invention for the oxidation agent of the pyrotechnic composition it is also possible to use polymers with such cage molecules as monomers. It is further also possible for the oxidation agent of the pyrotechnic composition to use a mixture of various ones of those fluorinated cage molecules, even of fluorinated cage molecules of the different specified kinds.

The advantages of the above-stated fluorinated spherical, carbocyclic cage molecules over the fluorine compounds conventionally used as oxidation agents such as polytetrafluoroethylene and graphite fluoride are based on the following considerations:

- On the one hand the fluorinated spherical, carbocyclic cage molecules as metastable molecules have a high internal stress which similarly to the cage molecules used as high energy-rich explosives, namely



octanitrocubane ( $C_8(NO_2)_8$ ) and hexanitrohexaazaisowurtzite ( $C_6H_6N_{12}O_{12}$ ), gives rise to high levels of combustion enthalpy.

- On the other hand those fluorinated cage molecules which can be interpreted as spherical tertiary alkyl fluorides have a considerably higher level of reactivity in relation to electron donors than unstressed tertiary alkyl fluorides with an ideal tetrahedron angle of  $109.5^\circ$  on the fluorine-bearing carbon atom, such as for example graphite fluoride [13]. This is relevant in relation to the present invention insofar as halophilic metals such as for example magnesium function as electron donors and the thermal reaction of magnesium with fluorocarbons takes place by way of electron transfer reactions in the condensed phase. That increased reactivity is also to be attributed to the high internal stress of the carbon structure and to the interaction, increasingly repelling with decreasing stress of the carbon structure from  $(CR^F)_4$  to  $(CR^F)_{60}$ , in respect of the fluorine atoms or perfluoroalkyl substituents respectively, and the C-F-bond attenuation which that entails.

- The formation heat of the fluorinated cage molecules according to the invention of for example  $C_{60}F_{48}$ , at 126 kJ per C-atom [11], is considerably lower than in the case of polytetrafluoroethylene, at 404 kJ per C-atom or in the case of poly(carbon monofluoride), at 195 kJ per C-atom.

- A further advantage of the specific fluorinated cage molecules over the previously used fluorohydrocarbons polytetrafluoroethylene and graphite fluoride lies finally in the physical properties thereof. Thus the fluorinated cage molecules according to the invention, in contrast to PTFE and graphite fluoride, can be dissolved in non-polar organic solvents such as toluene but also polar solvents such as tetrahydrofuran or acetone and in that way introduced into pyrotechnic compositions in molecular-disperse manner, which results in an improvement in the firing efficiency.

- In addition the specified fluorinated cage molecules can be undecomposedly sublimated. Those properties permit processing by gaseous phase deposition on metallic substrates and thus permit the production of metal/fluorinated cage molecules-composite materials.

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